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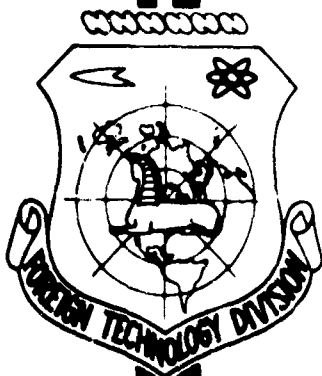
TRANSLATION

ELECTROCHEMICAL AND CORROSION BEHAVIOR OF STEEL AND NICKEL ELECTRODES IN SOLUTIONS OF SULFURIC ACID, SUBJECTED TO A REACTION OF γ -RADIATION

By

Ya. . Kolotyrkin, N. Ya. Bune and G. S. Tyruikov

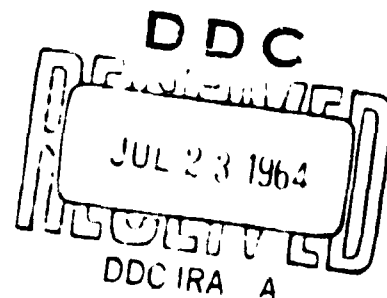
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ELECTROCHEMICAL AND CORROSION BEHAVIOR OF STEEL AND NICKEL
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Ya. M. Kolotyrkin, N. Ya. Bune and G. S. Tsiprikov

The result of reaction of radiation of high energies on aqueous solutions is, as is known, the decomposition of water with the formation of radicals and molecules, possessing restoring and oxidizing properties. In this respect, there occurs a change in oxidizing-restoring properties of the medium which must exert an influence on electrochemical and corrosion behavior of metals, placed in the solution; it is natural that a reaction from the radiation should be reflected in the first place in the magnitude of potential of electrode.

In this work was investigated electrochemical and corrosion behavior of stainless steel (type 18-8) and nickel in 1.0 N solutions H_2SO_4 with the reaction of a γ -radiation Co^{60} . Intensity of dose was 1.5×10^6 ev/ml.

The experiments were conducted in a glass instrument, analogous to that described in [1], in an atmosphere of purified nitrogen at room temperature.

In fig. 1 are presented curves, characterizing the change in potentials of steel electrodes in a process of irradiation. On axis of abscissas is plotted the time from the moment of beginning of reaction of irradiation, on axis of ordinates -- value of potential in volts relative to a normal hydrogen electrode.

Curve 1 pertains to electrode, covered by an air-oxidized film, curves 2 and 3 -- to electrodes, activated by preliminary cathode polarization. From the cited data it is clear that reaction from radiation in all cases results in a

displacement of the potential of towards positive values, in which the form of curves considerably depends on degree of activity of electrode. For activated electrodes, the displacement of potential became marked only after 2 to 3 hour after the beginning of the irradiation. At the same time, the more negative is the original value of potential and, consequently, the more active is the electrode, the later began the rapid displacement of the potential. For electrodes, covered with air-oxidized film, a rapid displacement of potential began almost immediately after the beginning of irradiation.

Experiments in studying of corrosion showed that in absence of radiation, the rate of dissolution of activated steel was equivalent to the current density, equal to approximately 10^{-5} a/cm². With an imposition of irradiation, the rate of dissolution of steel at first, prior to the rapid displacement of potential towards positive values, essentially did not vary. In attaining the final potentials (0.700-0.800v) rate of corrosion decreased so much that determining its magnitude by means of the weight method being applied in the work did not succeed even during prolonged experiments. In judging by the sensitivity of the final potential to external polarization, it was possible to conclude that the rate of dissolution in this case was equivalent 10^{-7} a/cm² and did not exceed this magnitude.

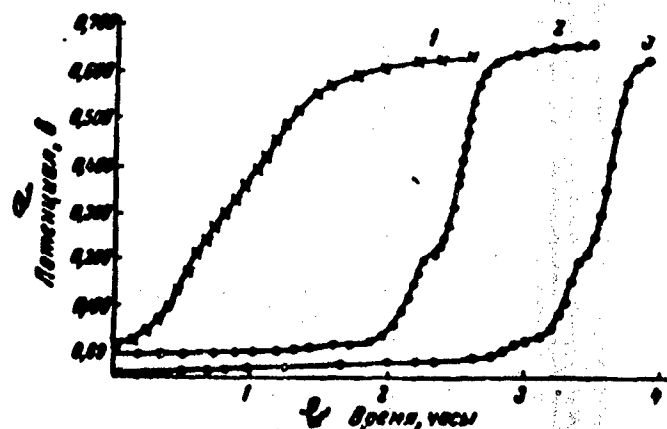


Fig. 1. Change in potential of an air-oxidized (1) and of activated (2,3) steel electrodes in process of irradiation. a) Potential; b) Time, hours.

For an evaluation of solubility steel there was derived a potentiostatic curve in a nonirradiated solution of sulphuric acid (curve 1, Fig. 2); the curves characterize the dependence of the stable rate of dissolution of an electrode on the potential in a broad region of the polarizations. The methodology of deriving such curves was published earlier [2, 3]. On axis of abscissas (Fig. 2) were plotted logarithms of the rate of dissolution in units of density of an electric current, on axis of ordinates, corresponding values of the potentials.

From the cited data it is clear that for steel of the investigated quality, there are several regions of polarizations differing by the observed dependence of a stable rate of dissolution on the potential.

As was shown previously, special value of potentiostatic curves consists in the fact that by means of them, on the basis of magnitude of potential, being established in the electrode in a given solution, it is possible to judge about rate of dissolution, by not resorting to a direct determination of the latter. Such a method of evaluating the dissolution is shown to be useful in those cases, when a direct determination of corrosion losses for these or other reasons is made difficult.

In a comparison of the curve, characterizing change of potential of a steel electrode under irradiation (curve 2, Fig. 2) with a potentiostatic curve, it is clear that for activated electrodes, an imposition of irradiation was accompanied by displacement of the potential from initial region of passivation, where rate of dissolution was equivalent 10^{-5} a/cm² in initial region of repassivation, where rate of dissolution did not exceed 10^{-7} a/cm². For electrodes, covered with an air-oxidized film, both prior to irradiation, and during radiation effect rate of dissolution remained insignificant, although in this case, its magnitude during imposition of irradiation somewhat decreased.

For an explanation of observed change of potential in process of irradiation,

we derived curves, characterizing the change of potential in time during polarization of electrode by constant anodic current in nonirradiation solutions (curves of charging). One of such curves, corresponding to a current density $2 \cdot 10^{-6} \text{ a/cm}^2$, is shown in Fig. 2. As can be seen from this figure, between the curve of charging 2 and radiation curve 3 there is great similarity.

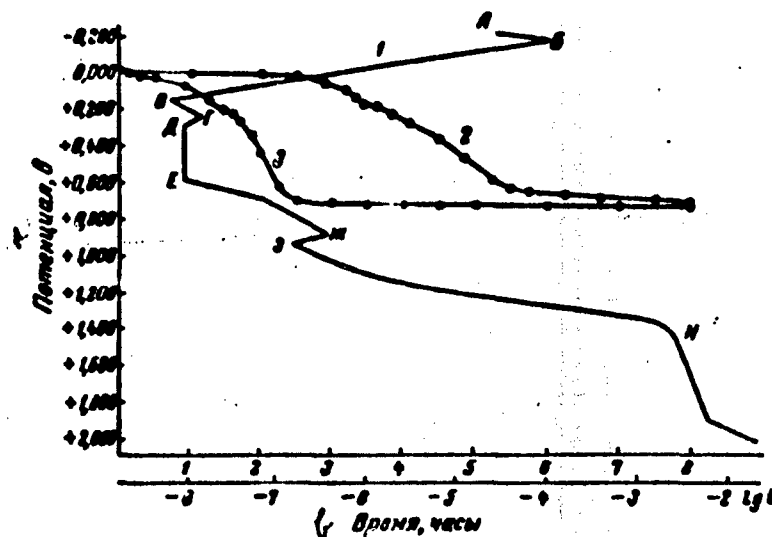


Fig. 2. 1-dependence of rate of stable dissolution of steel on potential in 1 N H_2SO_4 ; 2-change in potential of an activated electrode in process of irradiation; 3-curve of charging, derived during polarization of activated electrode by current $1 \cdot 10^{-6} \text{ a/cm}^2$. a) Potential i; b) Time, hours.

From the similarity of polarization and radiation curves it was possible to make the conclusion that the radiation effect on a steel electrode is equivalent to polarization its anodic current. Since the sole source of polarization in the system under analysis could be ionization of products radiolysis on the surface of the metal, then the obtained data attest, obviously, to the fact that on a steel electrode under conditions investigated by us to restoration of the oxidizing component proceeds at higher rates, than the oxidation of the restored.

In comparing the curves of charging, derived at different current densities

with the radiation curves it was possible to conclude that in our case the oxidizing radiation effect was equivalent to the current density, dose to $5 \cdot 10^{-7} - 1 \cdot 10^{-6}$ a/cm².

In the nickel electrode the reaction of γ -radiation also resulted in a displacement of the potential towards positive values. However, in this case magnitude of displacement (even in experiments lasting almost 20 hours) did not exceed 30-40 millivolts and was accompanied not by a decrease, but by an increase in the rate of dissolution by 2 to 3 times.

The difference in behavior of steel and nickel electrodes in an irradiated aqueous solutions becomes intelligible in a comparison of the potentiostatic curve of these metals. From the presented in Fig. 3 potentiostatic curve for nickel it is clear that region of active dissolution of this metal in the investigated solution extends up to + 0.150 i. Passivation of nickel could be realized only during a polarization of its currents, exceeding 10^{-2} a/cm², while for steel depending upon the state of its surface, for this was sufficient the polarization by currents of an order $10^{-5} - 10^{-7}$ a/cm². Thus, if for steel effective rate of restoration of the oxidizing components of "radiolysis" forming with a emissive power of radiation, was sufficient for its transition to a passive state, then for nickel it was by several orders less than the required magnitude. These results attest, obviously, to the fact that the corrosion behavior of metals in an irradiated aqueous solutions to a significant degree depends on their capability for passivation.

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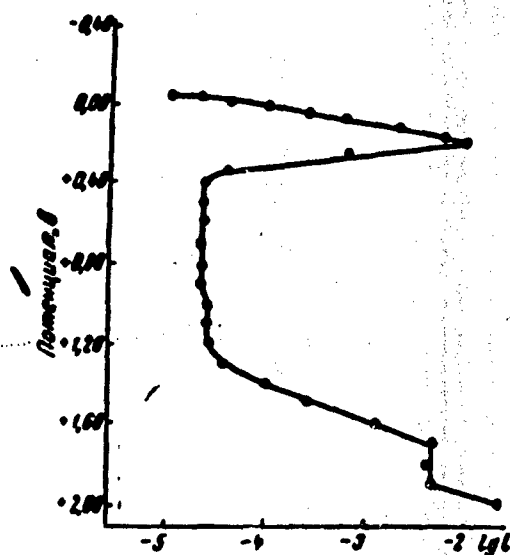


Fig. 3. Dependence of rate of stable dissolution of nickel on potential in 1 N H_2SO_4 . a) Potential i; b) $lg i$.

As our experiments showed, for steel and nickel there is observed also a nonuniform behavior of the potential after the ceasing of the radiation reaction. If in the case of nickel at the same time there occurred a rapid return of the potential to original value, then for steel the potential remained almost constant. The observable difference obviously, should be associated with the different nature of oxidizers present in the solution. The rapid disappearance of effect for nickel can be explained by the fact that the sole oxidizing components in this case were the shortly-lived products of "radiolysis", while in the presence of steel also to consider the presence in solution of more stable oxidizers, not disappearing after the cessation of irradiation. It was natural to assume that such oxidizers are the products of corrosion of steel, passing in solution in sufficiently large quantity on the region of active dissolution and then oxidized by products of the "radiolysis" of water.

For checking this assumption there was investigated reaction of γ -radiation on steel and platinum electrodes in a solution of sulphuric acid, containing:

products of corrosion of steel, and also ions Fe^{2+} . Corresponding data are presented in Fig. 4. Curves 3 and 4 in this figure refer to nonactivated electrodes, and while the first of them is obtained in a pure solution of sulphuric acid, but the second in the same solution, containing 0.001 g-equiv/l FeSO_4 . Curves 1 and 2 refer to activated electrodes, while the second of them was obtained in a pure solution of acid, but the first -- in the presence of products of corrosion in a quantity 0.18 g.

A comparison of these curves shows that for electrodes with identical state of the surface the presence in solution of ions of iron both directly added and also in the form of products of corrosion, results in an increase of the slopes of linear sections and to displacement of the final potential towards positive values that which attests to the increase in solution of the concentration of the oxidizer. This is associated, obviously, with the fact that in the presence of ions of bivalent iron in the solution occurs an interaction of them from oxidizing component of "radiolysis"; this results in a decrease in their reversible recombination of products of "radiolysis" and to an increase in total of stationary concentration of oxidizer in solution.

In connection with this one should note that, judging from our data, the oxidizers, appearing as a result of radiation decomposition of water, by its own electrochemical reaction to metals, in principle, do not differ from such type of oxidizers, as trivalent iron. At the same time, in particular, one can be convinced of the fact that curve 1 (Fig. 5), characterizing change in potential of an air-oxidized steel electrode in time in nonirradiated solution of sulphuric acid, containing a small quantity of trivalent iron is completely analogous with curves of charging, derived corresponding current densities, and with the radiation curves. As can be seen from Fig. 5, imposition of irradiation (at point A) resulted in a small additional displacement of potential in the direction of positive values.

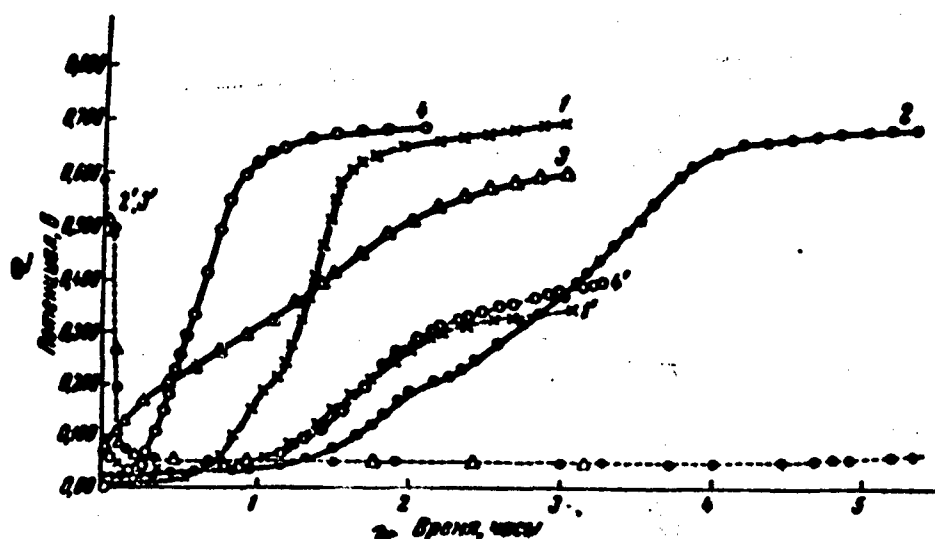


Fig. 4. Change during reaction of radiation of potential of activated (1, 2) and of air-oxidized (3,4) steel and platinum (1', 2', 3', 4') electrodes in a solution of pure acid (2,2' and 3,3'), in the products of corrosion in a quantity of 0.18g/l (1.1') and in a solution of $N H_2SO_4 + 0.001 \text{ g-equiv/l } FeSO_4$ (4.4)'. a) Potential i; b) time, hours.

For comparison in Fig. 4 and 5 there are presented also curves, characterizing behavior of the potential of platinum electrode, being found simultaneously with steel under corresponding conditions. As can be seen from the presented data, behavior of platinum very strongly differs from the behavior of steel. As, in solutions of pure acid (curves 2' and 3', Fig. 4) in accordance with results, obtained in [4], after several minutes after the imposition of irradiation the potential of platinum electrode acquired a value, near the potential of the reversible hydrogen electrode. In a solution, containing ions of iron (curves 1' and 4', Fig. 4 and curve 2, Fig. 5), the displacement of potential of platinum in the direction of negative values was observed only in the first period after imposition of irradiation later there occurred a displacement of potential in the direction positive values. However, also in this case, the final potential

of platinum had a larger negative value, than the potential of steel, although, as is seen in Fig. 5, in nonirradiated solutions, containing ions of trivalent iron a converse relationship took place.

The obtained data attests, obviously to the fact that metal, found in an irradiated solution, can be assumed as an ordinary irreversible oxidizing-restoring system. In this respect the dependence of the magnitude of stationary potential on the nature of metal becomes intelligible.

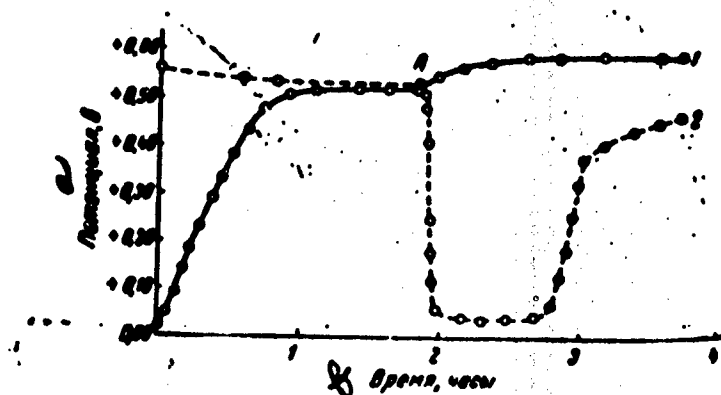


Fig. 5. Change of potential of steel (1) and platinum (2) in a solution of sulphuric acid, containing trivalent iron. a) Potential E ; b) Time, hours.

For reversible oxidizing-restoring system, the magnitude of potential being established only on nature and relationship of concentrations of the reacting substances. The change in nature of metal or the state of its surface is accompanied in this case by a symmetrical change of the constant, depending for a given reaction on the nature of the metal and the state of its surface and can result only in a change of the currents of exchange, but not of the value of the potential.

For irreversible systems, such as solutions containing products of "radiolysis" a symmetry in the change of these constants will not be observed,

and value of potential being established depend not only on nature and relationship of oxidizing and restoring components, but also on the nature of metal and the state of its surface.

In this respect, by considering the nature of oxidizing-restoring reactions, occurring in this case at the surface of electrode, it is possible to assume that the potential being established in metal with low overvoltage of hydrogen and high overvoltage of oxygen, will acquire in the irradiated aqueous solutions a greater negative value, than potential being established in metal with high overvoltage of hydrogen and low overvoltage of oxygen.

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